

MATERIALS AND METHODS FOR IMPRINT LITHOGRAPHY

TECHNICAL FIELD OF THE INVENTION

[0001] One or more embodiments of the present invention relate generally to imprint lithography. In particular, one or more embodiments of the present invention relate to materials and methods for imprint lithography.

BACKGROUND OF THE INVENTION

[0002] Micro-fabrication involves the fabrication of very small structures, for example, and without limitation, structures having features on the order of micro-meters or smaller. One area in which micro-fabrication has had a sizeable impact is in processing of integrated circuits. As the semiconductor processing industry continues to strive for larger production yields while increasing the circuits per unit area formed on a substrate, micro-fabrication becomes increasingly important since micro-fabrication provides greater process control while allowing a reduction in the minimum feature dimension of the structures formed. Other areas of development in which micro-fabrication have been employed include biotechnology, optical technology, mechanical systems and the like.

[0003] An exemplary micro-fabrication technique is disclosed in U.S. Patent No. 6,334,960 to Willson et al. In particular, the Willson et al. patent discloses a method of imprint lithography to form a relief pattern in a structure. The method includes providing a substrate having a transfer layer (typically spin-coated), and covering the transfer layer, in turn, with a low viscosity,

polymerizable (typically UV curable) fluid composition (typically in the form of droplets). The method further includes mechanically contacting an imprint template or mold having a relief structure with the polymerizable fluid composition wherein the polymerizable fluid composition fills a gap between the imprint template and the substrate and fills the relief structure of the imprint template. Next, the method includes subjecting the polymerizable fluid composition to conditions to solidify and to polymerize the same (typically, exposing the polymerizable fluid composition to UV to crosslink it), thereby forming a solidified polymeric material on the transfer layer that contains a relief structure complimentary to that of the imprint template. Next, the method includes separating the imprint template from the substrate to leave solid polymeric material on the substrate, which solid polymeric material includes a relief pattern in the form of the complimentary relief structure. Next, the solidified polymeric material and the transfer layer are subjected to an environment to selectively etch the transfer layer relative to the solidified polymeric material to form a relief image in the transfer layer.

[0004] The following issues that relate to selective adhesion of the solidified polymeric material to different surfaces are typically considered when one develops a method and/or a material useful in forming fine-feature relief patterns in the solidified polymeric material. First, the solidified polymeric material ought to adhere well to the transfer layer on the substrate, and second, it ought to be easily released from the surface of the imprint template. These issues are typically referred to as

release characteristics and selective/preferential adhesion, and if they are satisfied, the relief pattern recorded in the solidified polymeric material will not be distorted during separation of the imprint template from the substrate. To improve release characteristics, Willson et al. teaches forming a release layer on the surface of the imprint template, which release layer is typically hydrophobic and/or has low surface energy. Such a release layer will provide a weak boundary layer between the imprint template and the solidified polymeric material. This type of release layer is referred to, for purposes of the present discussion, as an *a priori* release layer, i.e., a release layer that is solidified to the surface of the imprint template.

[0005] Another prior art approach to improving the release characteristics is described by Bender et al. in "Multiple Imprinting in UV-based Nanoimprint Lithography: Related Material Issues," *Microelectronic Engineering* 61-62 (2002), pp. 407-413. Specifically, Bender et al. utilizes an imprint template having an *a priori* release layer in conjunction with a fluorine-containing UV curable material. To that end, a UV curable layer is applied to a substrate by spin-coating a 200 cps UV curable fluid to form a UV curable layer. The UV curable layer is enriched with fluorine groups to improve its release characteristics.

[0006] *A priori* release layers, however, typically have a limited operational life. As a result, a single imprint template needs to be coated multiple times with an *a priori* release layer during imprint processing. This can result in several hours of down-time for a given imprint template, thereby reducing throughput. Additionally, the molecular

structure of the *a priori* release layer may limit the minimization of the minimum feature dimension that is printed.

[0007] One measure of imprint lithography quality relates to feature filling. As is well known, sufficient wetting, along with other factors, ensures feature filling, and thereby prevents voids. To test one imprint lithography method and imprint material, we made imprints utilizing a 25 mm x 25 mm imprint template having reasonably well scattered features (i.e., the features were scattered widely enough to avoid repeated high density patterns -- less than 10% of the template surface was covered by features) with feature heights of about 100 nm to provide imprints wherein a typical residual layer thickness was about 50-100 nm (as is well known, solidified polymeric material disposed between features is typically referred to as a residual layer). In particular, we were able to provide void free imprints utilizing the following method steps: (a) pre-cleaning the surface of the imprint template by dipping its surface in a 2.5:1 solution of H_2SO_4 and H_2O_2 ; (b) further pre-treating the surface of the imprint template with a spray of diluted surfactant solution consisting of 0.1% FSO-100 in isopropyl alcohol ("IPA") where FSO-100 is a surfactant that is available under the designation ZONYL[®] FSO-100 from DUPONT[™] (FSO-100 has a general structure of R_1R_2 where $\text{R}_1 = \text{F}(\text{CF}_2\text{CF}_2)_Y$, with Y being in a range of 1 to 7, inclusive, and $\text{R}_2 = \text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_X\text{H}$, where X is in a range of 0 to 15, inclusive); (c) purging a gap between the imprint template and the substrate using an ~ 5 psi Helium purge; (d) depositing a pattern of substantially equidistant droplets

of the following imprinting fluid on the surface of the substrate (where each component is listed by weight): (i) acryloxymethylpentamethyldisiloxane (37 gm) which is available under the designation XG-1064 from Gelest, Inc. of Morrisville, Pennsylvania, (ii) isobornyl acrylate ("IBOA") (42 gm) which is available under the designation SR 506 from Aldrich Chemical Company of Milwaukee, Wisconsin, (iii) ethylene glycol diacrylate (18 gm) which is available under the designation EGDA from Aldrich Chemical Company of Milwaukee, Wisconsin, (iv) a UV photoinitiator, i.e., 2-hydroxy-2-methyl-1-phenyl-propan-1-one (3 gm) which is available under the designation Darocur 1173 from CIBA® of Tarrytown, New York), and (v) FSO-100 (0.5 gm); and (e) performing imprint lithography steps as described above. In this example, the substrate was covered with a transfer layer of a cross-linked BARC material (as is well known, BARC or "bottom antireflective coating" is an organic antireflective coating that is typically produced by a spin-on process). The BARC layer was used to prevent intermixing between the imprinting material and the transfer layer, which intermixing may be particularly problematic when using an imprinting material comprised of low viscosity acrylate components because such components have solvency toward many polymers. Such intermixing may cause problems, such as, for example, and without limitation, distortion of features when the imprint template is separated from the substrate after exposure to polymerizing radiation. In particular, this can be problematic when feature thicknesses are as small as 50 nm to 100 nm.

[0008] Despite the above-described successful imprinting, material voids were observed when we imprinted a high feature density imprint template using the above-described imprinting method. Two important differences between the high feature density imprint template and the above-described imprint template were that the feature density was much higher (for example, and without limitation, about 30% to about 40% of the surface of the template was covered by features in the high feature density imprint template) and the feature height of the high feature density imprint template was much higher, i.e., a height of 200 nm as compared to a height of 100 nm.

[0009] In light of the above, there is a need for imprinting methods and materials for use in imprint lithography that overcome one or more of the above-identified problems.

SUMMARY OF THE INVENTION

[0010] One or more embodiments of the present invention satisfy one or more of the above-identified needs in the art. In particular, one embodiment of the present invention is a method of imprint lithography that comprises depositing an imprinting material on a substrate; varying release properties associated with an imprint template by contacting a solution including imprinting materials and a polymeric fluorinated surfactant; and energizing the imprinting materials to cause a solid material to be produced therefrom. Specifically, it was recognized that employing a polymeric surfactant containing solution to a surface of an imprint template substantially reduced, if not prevented, formation of voids during imprinting. To

that end, an exemplary polymeric fluorinated surfactant is 3M™ Novec™ Fluorosurfactant FC-4432. Specifically, it was found that by including in the polymeric fluorinated surfactant in a solution containing imprinting material, the desired release and wetting properties of the imprint template may be established. In this manner, the imprint template may be efficiently wetted with the imprint material, while provided with the desired release properties to reduce, if not prevent, distortions in the pattern recorded in the solidified imprint layer upon separation of the imprint template therefrom. Further, by including the polymeric fluorinated surfactant in the imprinting material it was found the surface energy associated with the imprint template may be regenerated during imprint to maintain the desired release and wetting properties. In accordance with another embodiment, a pre-treatment of the imprint template may be undertaken to coat the imprint template with a polymeric fluorinate surfactant before contacting the imprint material containing solution. In yet another embodiment of the present invention is an imprinting material that includes a polymeric fluorinated surfactant, such as 3M™ Novec™ Fluorosurfactant FC-4432.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG. 1 is a perspective view of a lithographic system useful in carrying out one or more embodiments of the present invention;

[0012] FIG. 2 is a simplified elevation view of a lithographic system shown in FIG. 1;

[0013] FIG. 3 is a simplified representation of material from which an imprinting layer, shown in FIG. 2, is comprised before being polymerized and cross-linked;

[0014] FIG. 4 is a simplified representation of cross-linked polymer material into which the material shown in FIG. 3 is transformed after being subjected to radiation;

[0015] FIG. 5 is a simplified elevation view of a mold spaced-apart from the imprinting layer, shown in FIG. 1, after patterning of the imprinting layer; and

[0016] FIG. 6 is a simplified elevation view of imprint material disposed on a substrate in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0017] FIG. 1 shows lithographic system 10 that may be used to carry out imprint lithography in accordance with one or more embodiments of the present invention and utilizing imprinting materials fabricated in accordance with one or more embodiments of the present invention. As shown in FIG. 1, system 10 includes a pair of spaced-apart bridge supports 12 having bridge 14 and stage support 16 extending therebetween. As further shown in FIG. 1, bridge 14 and stage support 16 are spaced-apart. Imprint head 18 is coupled to bridge 14, and extends from bridge 14 toward stage support 16. Motion stage 20 is disposed upon stage support 16 to face imprint head, and motion stage 20 is configured to move with respect to stage support 16 along X- and Y-axes. Radiation source 22 is coupled to system 10 to impinge actinic radiation upon motion stage 20. As further shown in FIG. 1, radiation source 22 is coupled to

bridge 14, and includes power generator 23 connected to radiation source 22.

[0018] Referring to FIGS. 1 and 2, connected to imprint head 18 is imprint template 26 having mold 28 thereon. Mold 28 includes a plurality of features defined by a plurality of spaced-apart recessions 28a and protrusions 28b. The plurality of features defines an original pattern that is to be transferred into substrate 31 positioned on motion stage 20. Substrate 31 may comprise a bare wafer or a wafer with one or more layers disposed thereon. To that end, imprint head 18 is adapted to move along the Z-axis and vary a distance "d" between mold 28 and substrate 31. In this manner, features on mold 28 may be imprinted into a conformable region of substrate 31, discussed more fully below. Radiation source 22 is located so that mold 28 is positioned between radiation source 22 and substrate 31. As a result, mold 28 is fabricated from material that allows it to be substantially transparent to the radiation produced by radiation source 22.

[0019] Referring to FIGS. 2 and 3, a conformable region, such as imprinting layer 34, is disposed on a portion of surface 32 that presents a substantially planar profile. It should be understood that the conformable region may be formed using any known technique to produce conformable material on surface 32, such as a hot embossing process disclosed in United States patent number 5,772,905 to Chou, which is incorporated by reference in its entirety herein, or a laser assisted direct imprinting (LADI) process of the type described by Chou et al. in *Ultrafast and Direct Imprint of Nanostructures in Silicon*, Nature, Col. 417, pp. 835-837, June 2002. In accordance with one embodiment of

the present invention, the conformable region consists of imprinting layer 34 being deposited as a plurality of spaced-apart discrete droplets 36 of material 36a on substrate 31, discussed more fully below. Imprinting layer 34 is formed from a material 36a that may be selectively polymerized and cross-linked to record the original pattern therein, defining a recorded pattern. Material 36a is shown in FIG. 4 as being cross-linked at points 36b, forming cross-linked polymer material 36c.

[0020] Referring to FIGS. 2, 3 and 5, the pattern recorded in imprinting layer 34 is produced, in part, by mechanical contact with mold 28. To that end, imprint head 18 reduces the distance "d" to allow imprinting layer 34 to come into mechanical contact with mold 28, spreading droplets 36 so as to form imprinting layer 34 with a contiguous formation of material 36a over surface 32. In one embodiment, distance "d" is reduced to allow sub-portions 34a of imprinting layer 34 to ingress into and fill recessions 28a.

[0021] To facilitate filling of recessions 28a, material 36a is provided with the requisite properties to completely fill recessions 28a while covering surface 32 with a contiguous formation of material 36a. In accordance with one embodiment of the present invention, sub-portions 34b of imprinting layer 34 in superimposition with protrusions 28b remain after the desired, usually minimum distance "d", has been reached, leaving sub-portions 34a with a thickness t_1 , and sub-portions 34b with a thickness t_2 . Thicknesses "t₁" and "t₂" may be any thickness desired, dependent upon the application.

[0022] Referring to FIGS. 2, 3 and 4, after a desired distance "d" has been reached, radiation source 22 produces actinic radiation that polymerizes and cross-links material 36a, forming polymer material 36c in which a substantial portion thereof is cross-linked. As a result, material 36a transforms to polymer material 36c, which is a solid, forming imprinting layer 134, shown in FIG. 5.

Specifically, polymer material 36c is solidified to provide side 34c of imprinting layer 134 with a shape conforming to a shape of a surface 28c of mold 28, with imprinting layer 134 having recesses 30 (the bottom of the recesses may be referred to as a residual layer). After imprinting layer 134 is transformed to consist of polymer material 36c, shown in FIG. 4, imprint head 18, shown in FIG. 2, is moved to increase distance "d" so that mold 28 and imprinting layer 134 are spaced-apart.

[0023] Referring to FIG. 5, additional processing may be employed to complete the patterning of substrate 31. For example, substrate 31 and imprinting layer 134 may be etched to transfer the pattern of imprinting layer 134 into substrate 31, providing a patterned surface (not shown). To facilitate etching, the material from which imprinting layer 134 is formed may be varied to define a relative etch rate with respect to substrate 31, as desired.

[0024] To that end, etching may be performed in a two-step process. S.C. Johnson, T.C. Bailey, M.D. Dickey, B.J. Smith, E.K. Kim, A.T. Jamieson, N.A. Stacey, J.G. Ekerdt, and C.G. Willson describe suitable etch processes in an article entitled "Advances in Step and Flash Imprint Lithography" SPIE Microlithography Conference, February 2003, which article is available on the Internet at

www.molecularimprints.com, and which article is incorporated by reference herein. As set forth in the article, the first etch step, referred to as a "break-through etch," anisotropically removes residual cross-linked material 134 to break through to an underlying transfer layer (in this respect, better etch selectivity is enabled by keeping the residual layer thin). The second etch step, referred to as a "transfer etch," uses the remaining pattern in cross-linked material 134 as an etch mask to transfer the pattern into the underlying transfer layer. In one embodiment, silicon in cross-link material 134, and lack of silicon in the transfer layer, provides etch selectivity therebetween. In such an embodiment, the etching may be done in a LAM Research 9400SE obtained from Lam Research, Inc. of Fremont, California. For example, and without limitation, a halogen "breakthrough etch" may be utilized which comprises an anisotropic halogen reactive ion etch ("RIE") rich in fluorine, i.e., wherein at least one of the precursors was a fluorine-containing material (for example, and without limitation, a combination of CHF_3 and O_2 , where the organosilicon nature of cross-linked material 134 may call for the use of a halogen gas). Other suitable halogen compounds include, for example, and without limitation, CF_4 . This etch is similar to a standard SiO_2 etch performed in modern integrated circuit processing. Next, an anisotropic oxygen reactive ion etch may be used to transfer the features to underlying substrate 31 wherein the remaining silicon containing features serve as an etch mask to transfer the pattern to underlying substrate 31. The "transfer etch" may be achieved, for example, and without limitation, with a standard, anisotropic, oxygen

RIE processing tool. However, in general, any suitable etch process may be employed dependent upon the etch rate desired and the underlying constituents that form substrate 31 and imprinting layer 134. Exemplary etch processes may include plasma etching, reactive ion etching, chemical wet etching and the like.

[0025] Referring to both FIGS. 1 and 2, exemplary radiation source 22 may produce ultraviolet radiation; however, any known radiation source may be employed. The selection of radiation employed to initiate the polymerization of the material in imprinting layer 34 is known to one skilled in the art and typically depends on the specific application which is desired. Furthermore, the plurality of features on mold 28 are shown as recessions 28a extending along a direction parallel to protrusions 28b that provide a cross-section of mold 28 with a shape of a battlement. However, recessions 28a and protrusions 28b may correspond to virtually any feature required to create an integrated circuit and may be as small as a few tenths of nanometers.

[0026] Referring to FIGS. 1, 2 and 5, the pattern produced by the present patterning technique may be transferred into substrate 31 to provide features having aspect ratios as great as 30:1. To that end, one embodiment of mold 28 has recessions 28a defining an aspect ratio in a range of 1:1 to 10:1. Specifically, protrusions 28b have a width W_1 in a range of about 10 nm to about 5000 μm , and recessions 28a have a width W_2 in a range of 10 nm to about 5000 μm . As a result, mold 28 and/or template 26, may be formed from various conventional materials, such as, but not limited to, fused-silica, quartz, silicon, organic

polymers, siloxane polymers, borosilicate glass, fluorocarbon polymers, metal, hardened sapphire and the like.

[0027] Referring to FIGS. 1, 2 and 3, the characteristics of material 36a are important to efficiently pattern substrate 31 in light of the deposition process employed. As mentioned above, material 36a is deposited on substrate 31 as a plurality of discrete and spaced-apart droplets 36. The combined volume of droplets 36 is such that the material 36a is distributed appropriately over an area of surface 32 where imprinting layer 34 is to be formed. As a result, imprinting layer 34 is spread and patterned concurrently, with the pattern being subsequently set into imprinting layer 34 by exposure to radiation, such as ultraviolet radiation. As a result of the deposition process, it is desired that material 36a have certain characteristics to facilitate rapid and even spreading of material 36a in droplets 36 over surface 32 so that all thicknesses t_1 are substantially uniform and all thicknesses t_2 are substantially uniform. The desirable characteristics include having a low viscosity, for example, and without limitation, in a range of about 0.5 to about 10 centipoise (cps), as well as the ability to wet surface of substrate 31 and mold 28 and to avoid subsequent pit or hole formation after polymerization. Preferably, the viscosity is in a range of 0.5 to 5 cps. With these characteristics satisfied, imprinting layer 34 may be made sufficiently thin while avoiding formation of pits or holes in the thinner regions, such as sub-portions 34b, shown in FIG. 5.

[0028] The constituent components that form material 36a to provide the aforementioned characteristics may differ. This results from substrate 31 being formed from a number of different materials. As a result, the chemical composition of surface 32 varies dependent upon the material from which substrate 31 is formed. For example, substrate 31 may be formed from silicon, plastics, gallium arsenide, mercury telluride, and composites thereof. Additionally, substrate 31 may include one or more layers in sub-portion 34b, for example, dielectric layer, metal layer, semiconductor layer, planarization layer and the like.

[0029] Referring to Figs. 2, 3 and 4, it is desired, however, that material 36a include components to provide mold 28 with surface characteristics such that mold 28 may satisfy two --seemingly contradictory-- surface energy requirements. Specifically, once material 36a is solidified into material 36c, mold 28 should have the requisite surface energy to release from solidified material 36c so as to minimize distortions in the pattern recorded in solidified material 36c. Additionally, to ensure efficient filling of features of mold 28, it is desired that the surface of mold 28 have a sufficiently high surface energy to facilitate wetting of mold 28 with imprinting material 36a.

[0030] As was discussed in the Background of the Invention, in accordance with one particular method of imprinting, one manner in which the two aforementioned requirements for mold surface were balanced involved pre-treating the surface of mold 28 and including a surfactant in imprinting material. To that end, a pre-treatment

solution including isopropyl alcohol ("IPA") and a surfactant consisting of 0.1% FSO-100 was employed. The imprinting material also included the surfactant FSO-100. FSO-100 is available under the designation ZONYL[®] FSO-100 from DUPONT[™] and has a general structure of R_1R_2 where $R_1 = F(CF_2CF_2)_Y$, with Y being in a range of 1 to 7, inclusive, and $R_2 = CH_2CH_2O(CH_2CH_2O)_XH$, where X is in a range of 0 to 15, inclusive. FSO-100 is a fluorinated surfactant having a molecular weight of about 600, and it aligns efficiently at the surface of the imprint template with hydrophobic $-CF_3$ groups projecting towards the surface of the imprint template. Such alignment is promoted by pre-cleaning the surface (prior to pre-treatment utilizing a surfactant solution consisting of 0.1% FSO-100 in IPA) to create silanol functional groups on the surface. However, the present invention provides an improved method and material that substantially reduces, if not prevents, void formation when imprinting high density features having a height of about 200 nm.

[0031] This is achieved, in part, by employing a polymeric fluorinated surfactant. An exemplary polymeric fluorinated surfactant is available under the designation 3M[™] Novec[™] Fluorosurfactant FC-4432 (hereafter referred to as FC-4432) from 3M Company of St. Paul, Minnesota in the manner described in detail below to provide an imprinting material and methods for imprint lithography. FC-4432 is a non-ionic polymeric fluorochemical surfactant belonging to a class of coating additives which provide low surface tensions in organic coating systems. The composition of FC-4432 is 87% polymeric fluorochemical actives, 7% non-fluorochemical actives, 5% 1-methyl-2-pyrudione, and <1%

toluene. FC-4432 is a wetting, leveling and flow control agent for radiation curable polymer coating systems, and continues to be active throughout the curing process. FC-4432 is the first in a new line of fluorochemical surfactants from the 3M Company based on perfluorosulfate (PFBS), where PFBS refers collectively to perfluorobutane sulfonyl compounds including perfluorobutane sulfonates. In addition, such PFBS-based surfactants with only four perfluorinated carbon atoms offer improved environmental properties. The molecular weight of FC-4432 is about 4000, and because of its higher molecular weight than that of FSO-100, the fluorinated groups of FC-4432 align differently at the surface of an imprint template than those in FSO-100. In particular, besides $-CF_3$ groups of FSO-100, FC-4432 has a higher percentage of $-CF_2$ groups situated at the surface when compared to FSO-100. Because a $-CF_2$ group provides a higher surface energy than a $-CF_3$ group, the presence of a higher percentage of $-CF_2$ groups in FC-4432 at template surface provides a material having better wetting than FS-100. However, despite its higher surface energy, a $-CF_2$ - group is hydrophobic enough so that its use produces a material having a good release property. In addition, it is believed that the higher molecular weight of FC-4432 (when compared to that of FSO-100) causes FC-4432 to act like a loosely packed coil structure that results in more porous molecular packing of surfactant molecules at the surface of the imprint template. It is further believed that this coil structure helps enhance wetting over that provided by FSO-100, and in addition to that provided by the presence of a higher percentage of surface $-CF_2$ groups in FC-4432 when compared to FSO-100.

[0032] An exemplary composition for material 36a that utilizes the surfactant FC-4432 is produced by mixing (with exemplary proportions being given in weight): (i) acryloxymethylpentamethyldisiloxane (for example, and without limitation, about 37 gm) which is available under the designation XG-1064 from Gelest, Inc. of Morrisville, Pennsylvania, (ii) isobornyl acrylate ("IBOA") (for example, and without limitation, about 42 gm) which is available under the designation SR 506 from Aldrich Chemical Company of Milwaukee, Wisconsin, (iii) ethylene glycol diacrylate (for example, and without limitation, about 18 gm) which is available under the designation EGDA from Aldrich Chemical Company of Milwaukee, Wisconsin, (iv) a UV photoinitiator, for example, and without limitation, 2-hydroxy-2-methyl-1-phenyl-propan-1-one (for example, and without limitation, about 3 gm) which is available under the designation Darocur 1173 from CIBA® of Tarrytown, New York), and (v) FC-4432 (for example, and without limitation, about 0.5 gm). The above-identified composition may also include stabilizers that are well known in the chemical art to increase the operational life of the composition. In a typical such embodiment, the surfactant comprises less than 1% of the imprinting material. However, the percentage of the surfactant may be greater than 1%.

[0033] An advantage provided by the above-described imprinting material is that it abrogates the need for an *a priori* release layer, i.e., a separate hydrophobic and/or low surface energy release layer disposed on imprint template 28 (as described in the Background of the Invention). Specifically, the imprinting material provides

desirable release properties to mold 28 and imprinting layer 34 so that material 36c, shown in FIG. 4, does not adhere to mold 28 with sufficient force to distort the pattern recorded therein.

[0034] Referring to FIG. 6, it is believed that surfactant molecules in droplets 36 of the imprinting material preferentially move toward the gas-liquid interface in less than about 1 sec. As such, it is believed that droplets 36 have a higher concentration of the surfactant in region 136 when compared with region 137 in which the polymerizable components are concentrated. It is believed that this is the result of an energy minimization process wherein the surfactant tends to move to the gas-liquid interface so that its hydrophobic end aligns towards the gas. For example, it is believed that the fluorinated, hydrophobic end of the FC-4432 (for example, comprised of $-CF_3$ and $-CF_2$ groups) is aligned to project out of the liquid and into the gas, and the hydrophilic end (i.e., $-OH$ and polar ethylene oxide groups) is aligned to project into the liquid. However, when the imprinting material contacts the surface of the imprint template, it is believed that exposed silanol bonds on the surface of the imprint template cause the hydrophilic end of the surfactant molecule to flip and to contact the exposed silanol bonds so that $-CF_3$ groups and $-CF_2$ groups face downward (i.e., outward from the surface of the imprint template) to enable adhesion reduction. It is further believed that surfactant lamella may also be formed at the surface of the imprint template, which lamella may comprise, for example, two (2) layers of surfactant molecules.

[0035] Referring to FIG. 2, an additional advantage provided by the above-described imprinting material is that the time required to wet mold 28 and, therefore, to spread droplets 36 may be reduced. Specifically, by abrogating the need to have an *a priori* release layer on mold 28, the surface of mold 28 may be provided with increased surface energy. Of course, the above-described imprinting material may be employed with an *a priori* release layer, such as those known in the prior art.

[0036] Another manner by which to improve the release properties of mold 28 includes conditioning the pattern of mold 28 by exposing the same to a conditioning mixture including an additive that will remain on mold 28 to reduce the surface energy of the mold surface. An exemplary additive is a surfactant.

[0037] The above-described imprinting material is useful in providing substantially void free imprint lithography utilizing high feature density and relatively tall feature height (for example, and without limitation, feature heights of about 200 nm) with residual layer thicknesses of 50-100 nm (note that providing thin residual layers requires low viscosity and small drops of imprinting material, i.e., viscosity below about 10 cps, and preferably below 5 cps, and drops at or below about 80 pico-liters).

[0038] The following describes a method for imprint lithography that utilizes one or more embodiments of the above-described imprinting material. As a first step, the surface of a quartz imprint template is pre-treated to create hydrophilic bonds at the surface, for example, and without limitation silanol (Si-OH) bonds. In accordance

with one or more embodiments of the present invention, the surface of the imprint template is dipped in a 2.5:1 solution of H_2SO_4 and H_2O_2 to hydrolyze the surface, i.e., to create silanol bonds at the surface. As a next step, the surface is further pre-treated by spraying the surface of the imprint template with a diluted FC-4432 solution (for example, and without limitation, 0.1% FC-4432 in IPA). Exposure of the surface of the imprint template may be achieved by virtually any method known in the art, including dipping the surface into a volume of pre-treatment solution, wiping the surface with a cloth saturated with pre-treatment solution, and spraying a stream of pre-treatment solution onto the surface. The IPA in the pre-treatment solution may be allowed to evaporate before using the mold 28. In this manner, the IPA facilitates removing undesired contaminants from the surface while leaving the surfactant. Because the surfactant includes a hydrophobic, fluorine-rich end, and a hydrophilic end, the silanol groups promote alignment of the surfactant so that the hydrophilic end "adsorbs" to the -OH end of the silanol groups, and the hydrophobic, fluorine-rich end points away from the surface. In a next step, a gap between the imprint template and the substrate may be purged of air (mainly O_2 and N_2) using, for example, and without limitation, an ~ 5 psi Helium purge. In a next step, the imprinting material containing the FC-4432 surfactant is applied to the substrate, for example, and without limitation, by placing a pattern of substantially equidistant droplets of imprinting material on the substrate, by spin-coating, or by any other method known to those of ordinary skill in the art. In this example, the

substrate was covered with a transfer layer whose top layer was a cross-linked BARC material (BARC or "bottom antireflective coating" is an organic antireflective coating that is typically produced by a spin-on process). The BARC layer was used to prevent intermixing between an imprinting material and the transfer layer, which intermixing may be particularly problematic when using an imprinting material comprised of low viscosity acrylate components because such components have solvency toward many polymers. Intermixing may cause problems such as, for example, and without limitation, distortion of features when an imprint template is separated from a substrate after exposure to polymerizing radiation. This can be particularly problematic when feature thicknesses are as small as 50 to 100 nm. Next, the familiar steps of imprint lithography are carried out, i.e., exposure to actinic radiation to polymerize the imprinting material; separation of the imprint template and the substrate; and selective etching to transfer the feature pattern to the substrate.

[0039] It is believed that the use of surface pre-treatments described above utilizing FC-4432 may be useful by itself in helping to provide substantially void free imprint lithography. For example, we have run experiments where the surface was pre-treated as described directly above, and wherein the imprinting material included FSO-100 as a surfactant rather than FC-4432. In this case a few void free imprints were made, but it is believed that as soon as the FC-4432 supplied to the surface of the imprint template by pre-treatment was abraded away, imprints having voids soon appeared.

[0040] It is believed that even when pre-treating the surface of the imprint template as described above utilizing FC-4432, FC-4432 adhered to the silanol groups on the surface of the imprint template ultimately is abraded away. However, as was described above, the FC-4432 contained in the imprinting material itself rapidly comes to the gas-liquid surface of the droplets, and the surface of the imprint template is re-coated with FC-4432 as a normal consequence of imprinting. As such, in accordance with one or more embodiments of the present invention, the pre-treatment step of applying the surfactant solution to the surface of the imprint template may be eliminated. In fact, in accordance with one or more further embodiments of the present invention, the imprint template may be contacted a few times with the imprinting material as a replacement for the pre-treatment step of applying the surfactant solution to the surface. In this manner, the use of the polymeric fluorinated surfactant, as discussed above, enables varying the surface characteristics of mold 28, and therefore template 26, to satisfying the two aforementioned contradictory surface energy requirements.

[0041] The embodiments of the present invention described above are exemplary. Many changes and modifications may be made to the disclosure recited above, while remaining within the scope of the invention. The scope of the invention should, therefore, be determined not with reference to the above description, but instead should be determined with reference to the appended claims along with their full scope of equivalents.